

PROGRESS REPORT

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MECHANICAL BEHAVIOR OF POLYCRYSTALLINE

NON-METALLICS AT ELEVATED TEMPERATURE

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MECHANICAL BEHAVIOR OF POLYCRYSTALLINE NON-METALLICS
AT ELEVATED TEMPERATURE
(SC-NGR-05-020-084)

I. Creep of Polycrystalline Sodium Chloride (Peter Burke)

Experimental results to date indicate that creep of polycrystalline sodium chloride is similar in many ways to creep of pure metals. This is a new and important observation. Typical creep curves for sodium chloride are shown in Figure 1. The curves show both primary and secondary or steady state regions of behavior.

Earlier tests by other authors⁽¹⁾ showed only steady state creep in polycrystalline sodium chloride at a temperature near the melting point. The creep rate was directly proportional to the creep stress. This type of creep behavior, in which little primary creep occurs and in which the creep rate is linearly dependent upon creep stress, is the so-called viscous, diffusional or Nabarro-Herring type of creep. Our tests indicate, however, that in polycrystalline sodium chloride, primary creep definitely occurs, the creep rate is proportional to stress to the fifth power, subgrains form during creep⁽²⁾ and the creep rate is apparently independent of grain size (165 to 2000 microns). These are all characteristics of the dislocation glide and climb mode of deformation that has been found to be the predominant mode of creep deformation for most pure polycrystalline metals.

The effects of temperature and stress on steady state creep of sodium chloride are shown in Figures 2 and 3. Data for two ranges of grain size are included; coarse (900-2000 microns) and fine (165-375 microns). The

empirical equation describing these curves is the same as that for many metals and is given by

$$\dot{\epsilon}_s = k (\sigma/E)^{4.5} \exp (-Q/RT)$$

where

$\dot{\epsilon}_s$ = steady state creep rate

k = a material constant related to stacking fault energy

σ = stress

E = Young's modulus of elasticity

Q = activation energy for creep

R = gas constant

T = absolute temperature

The activation energy, Q, is a measure of the temperature dependence of a process. Figure 4 shows the temperature dependence of steady state creep. A knee in the curve occurs at $\sim 530^\circ\text{C}$. Figure 5 shows the temperature dependence of diffusion of sodium and chlorine ions in sodium chloride. The slopes of the curves in Figures 4 and 5 give the activation energies for the processes of creep, sodium diffusion and chlorine diffusion in sodium chloride. Figure 6 shows the activation energies for these processes as a function of temperature.

The activation energy for creep above 530°C is substantially the same as that observed for chlorine ion diffusion in polycrystalline sodium chloride⁽⁴⁾. This leads to the conclusion that the rate controlling step in creep is chlorine ion diffusion, at least above 530°C .

Below 530°C there are no data for diffusion in polycrystals, but the activation energy for creep agrees fairly well with that for chlorine ion diffusion in crushed single crystals of high dislocation density. The

presence of dislocations below 530°C enhances the chlorine ion diffusion rate and lowers the activation energy. The dislocations either act at diffusion short circuits or else lead to the creation of surplus chlorine vacancies.

The activation energy for creep below 530°C also agrees fairly well with that observed for sodium diffusion in polycrystals at temperatures above 530°C. This correlation could lead one to conclude that sodium ion diffusion is creep rate controlling below 530°C. It seems unlikely, however, that the creep rate controlling process would change from chlorine ion diffusion to sodium ion diffusion at 530°C, because the diffusion coefficient observed for sodium diffusion at 530°C are at least ten times greater than those observed for chlorine diffusion. Furthermore, the activation energies observed for sodium diffusion in single crystals below 530°C are much lower than those observed for creep below 530°C. The most likely conclusion is that the rate controlling step in creep of polycrystalline sodium chloride is chlorine ion diffusion at all temperatures and that the activation energy for chlorine diffusion and hence creep is reduced by the presence of dislocations and/or grain boundaries at temperatures below 530°C.

Since creep in sodium chloride is controlled by chlorine ion diffusion, the empirical equation for creep may now be written as

$$\dot{\epsilon}_s = k' D (\sigma/E)^{4.5} \text{ or } \frac{\dot{\epsilon}_s}{D} = k' (\sigma/E)^{4.5}$$

where

$$D = D_0 \exp(-Q/RT)$$

= diffusion coefficient of chlorine ions in sodium chloride.

This equation has been extensively used to describe metallic behavior; here D is the self-diffusion coefficient for the metal.

Figure 7 shows a plot of $\dot{\epsilon}/D$ versus σ/E for sodium chloride and for aluminum.^{(3)*} The close correlation exhibited strengthens our impression that high temperature deformation of sodium chloride is similar to that of pure metals. It is of interest to note that the breakdown of the power law for creep of polycrystalline sodium chloride, that is, the up-sweep of the curve in Figure 7 at high creep rates, occurs at about $\dot{\epsilon}/D = 10^9 \text{ cm}^{-2}$. This value is in agreement with the values found for pure metals⁽¹¹⁾, including W, Cu, Al, Ni and α -Ti.

The observation that creep rates in sodium chloride are proportional to the diffusion coefficient of a chlorine indicates that the slowest diffusing species controls creep. Figure 5 shows that chlorine always diffuses more slowly than sodium. Deformation during creep occurs by the glide and climb of dislocations. Figure 8 shows a sketch of the Weertman model for glide and climb. Sketches of dislocations in metals and compounds are shown in Figure 9. For climb to occur, atoms must diffuse away from the dislocations. In sodium chloride both sodium and chlorine ions must diffuse away from dislocations simultaneously in order to maintain charge neutrality. Figure 10 shows the climb process occurring in a metal and in sodium chloride. The slow moving chlorine ions control

* The D values used for sodium chloride are indicated by squares in Figure 5. D values for temperatures above 530°C were taken to be equal to those measured for chlorine diffusion in 1000 micron grain size sodium chloride⁽⁴⁾. D values for temperatures below 530°C were obtained by drawing a line on the diffusion graph of slope equal to the activation energy experimentally observed for creep ($1.34\text{eV} = 30.7 \text{ Kcal/mol}$).

the rate at which climb can occur and hence the rate at which deformation occurs.

II. Creep of polycrystalline NaCl-KCl solid solutions (Roger Cannon)

During the last six months equipment has been perfected for producing samples of sodium chloride in solid solution with potassium chloride and most of the samples have been fabricated.

The procedure for producing samples is first to cast a billet from a mixture of the powders. This procedure ensures good mixing in the sample. This billet is then extruded into a rod form. The rod is cut up to sample length and the ends are polished.

Several problems were encountered in casting billets. The castings clung to the sides of the carbon die which made them difficult to remove and caused them to break up. By polishing the sides of the die and making a screw out type bottom, most of the problems were solved.

Since the carbon die must fit in a horizontal tube furnace it could not be very tall. Compacting the powders before casting made it possible to cast a larger billet.

Extrusion of solid solution sodium chloride-potassium chloride is very difficult, While making the second extrusion the die became so badly scored that the outer cylinder cracked while trying to remove the shafts. A new stronger die has now been made which works well. It was also necessary to make up a new larger furnace which would fit around the extrusion die.

While waiting for the die to be machined an attempt was made to produce fine grained samples of potassium chloride. In order to maintain a fine grain size, a tenth of a per cent of 0.1 micron aluminum oxide was

added. The one creep test completed showed a creep rate within a factor of two of that for sodium chloride at the same temperature and stress. The grain size did not remain small, however, but grew to approximately 200 microns during the test. A possible explanation for such severe grain growth is that the aluminum oxide settled to the bottom of the casting and was not present to a great extent in this particular sample. Some other method of fabrication will be necessary to retain the aluminum oxide in the sample.

Results on the constant stress creep tests run thus far on samples of fifty per cent sodium chloride-fifty per cent potassium chloride show no steady state creep. A typical creep curve for the solid solution alloy tested is shown in Figure 9. The creep rate increases with time as is the case with tertiary creep. The upsweep, however, may not be a creep phenomenon. Samples were highly cracked after the creep tests. The increase in creep rate may have been due to the formation and propagation of cracks.

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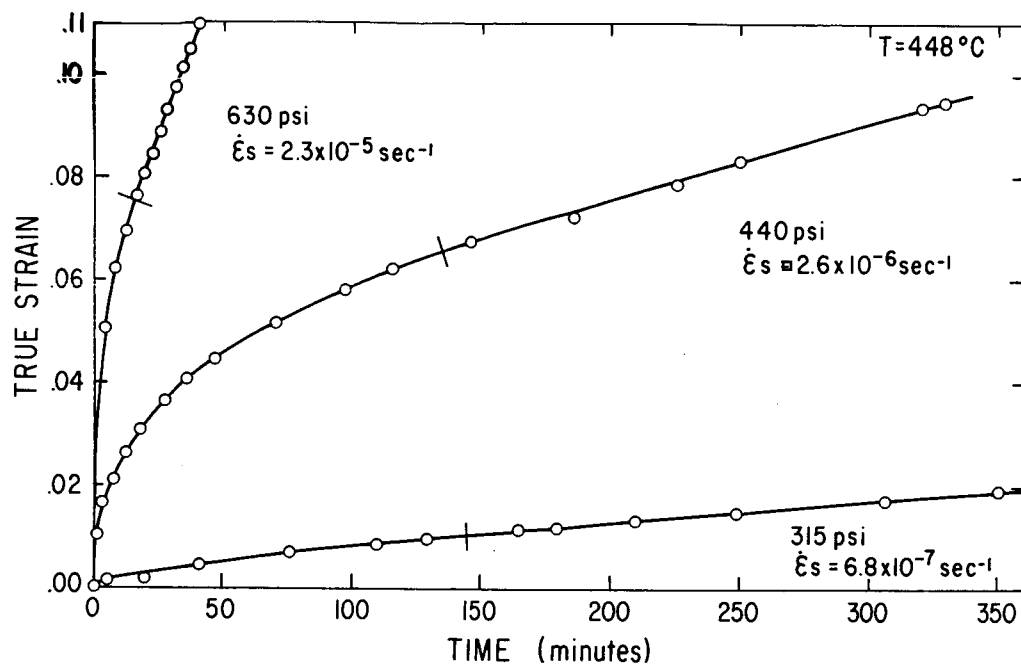


Figure 1. Typical creep curves for polycrystalline sodium chloride, showing primary and steady state creep.

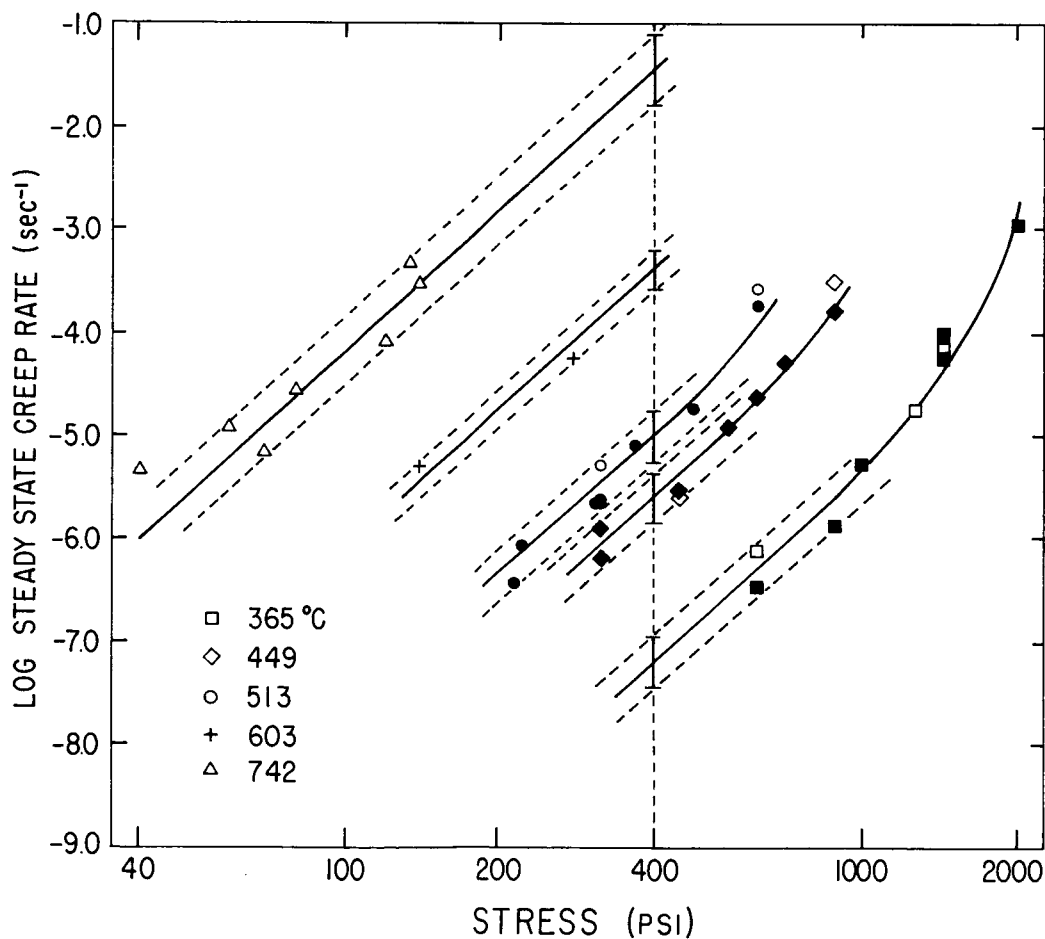


Figure 2. Effect of stress and temperature on steady state creep rate of sodium chloride.

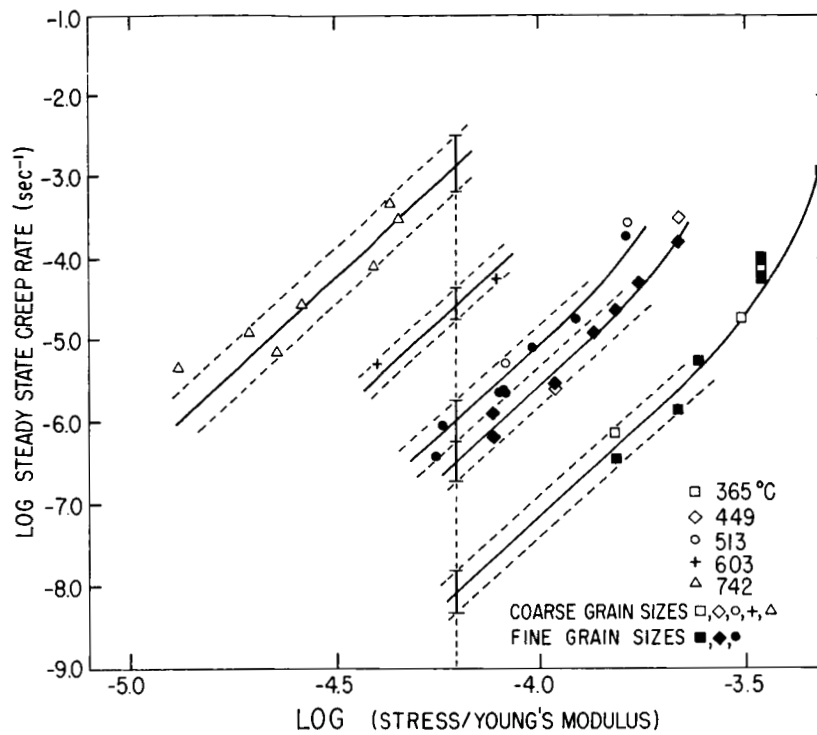


Figure 3. Effect of stress and temperature on steady state creep rate of sodium chloride, corrected for temperature variation of Young's Modulus of Elasticity.

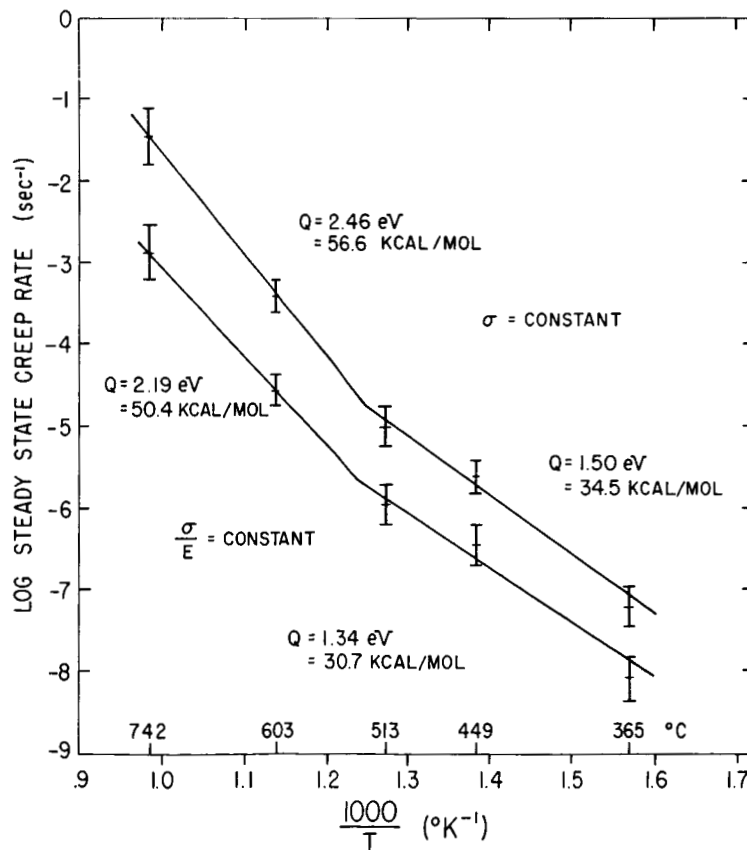


Figure 4. Temperature dependence of steady state creep rate.

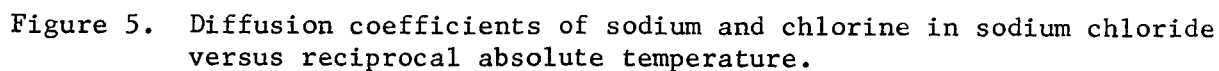


Figure 5. Diffusion coefficients of sodium and chlorine in sodium chloride versus reciprocal absolute temperature.

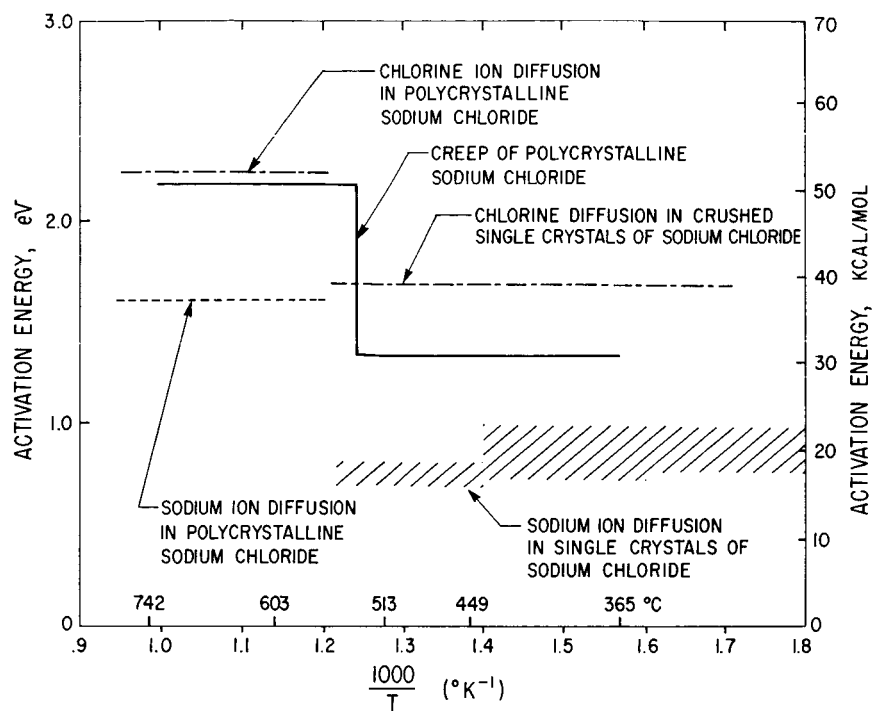


Figure 6. Experimentally determined activation energies for sodium diffusion, chlorine diffusion and creep in sodium chloride as a function of temperature.

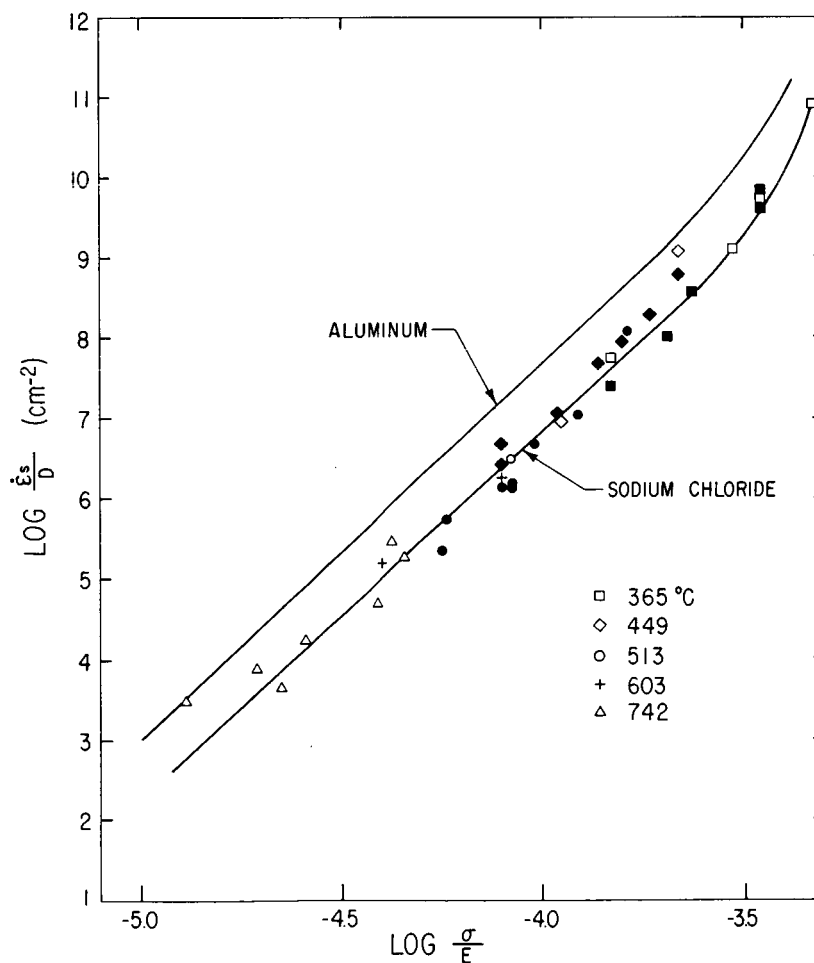


Figure 7. Plot of $\dot{\epsilon}_s/D$ versus σ/E , showing similarity between sodium chloride and aluminum.

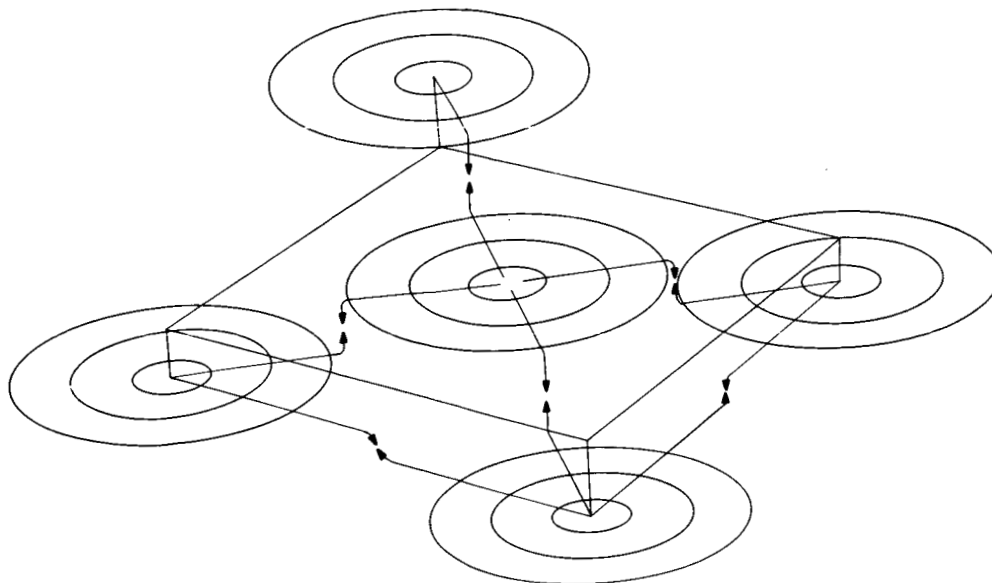


Figure 8. Sketch showing Weertman model for dislocation glide and climb controlled creep. Dislocation climb occurs in the direction of the arrows.

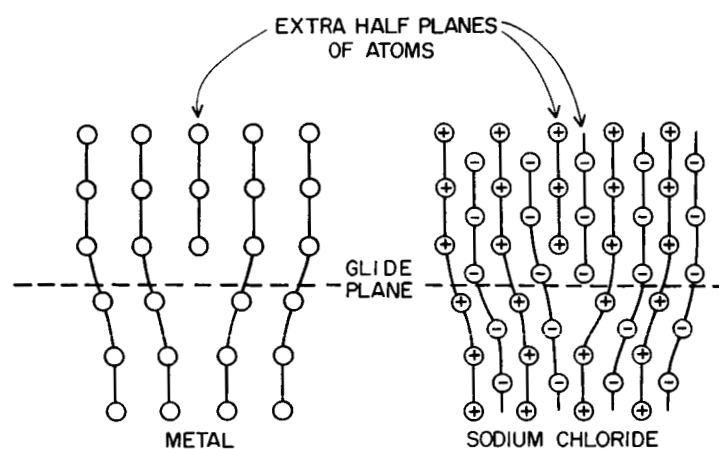


Figure 9. Sketch of edge dislocations in metals and in sodium chloride.

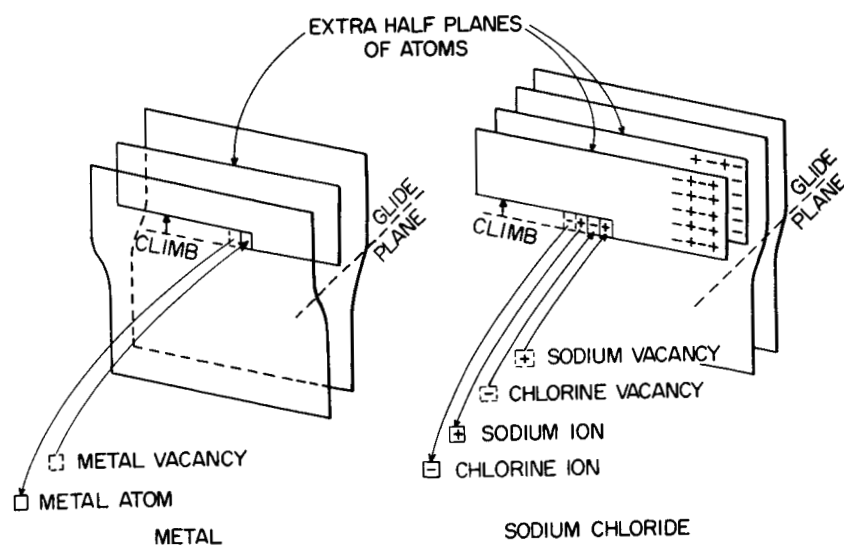


Figure 10. Sketch illustrating climb of edge dislocations in metals and in sodium chloride.

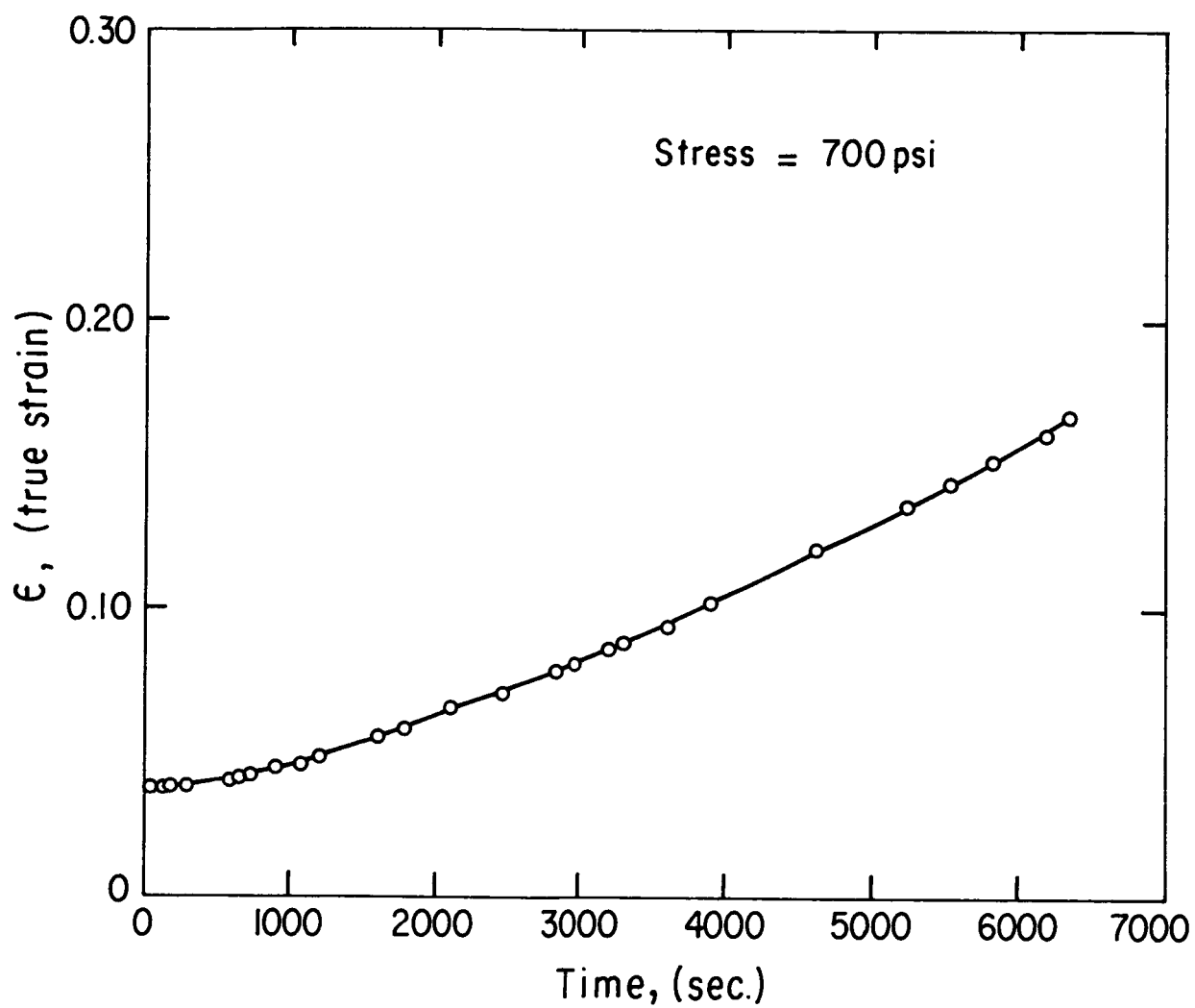


Figure 11. Creep strain versus time of polycrystalline NaCl-KCl solid solution. Temperature is 510°C.